

**Prof. T. L. Cottrell** (*University of Edinburgh*) said: If Prof. Porter's radical-molecule complex theory is correct, then there should surely be a detectable equilibrium concentration of  $I_3$  molecules in iodine vapour. The vapour density data of Perlman and Rollefson<sup>1</sup> which lead to an accurate value of the heat of dissociation of iodine do not suggest that any  $I_3$  is present. I should like to ask Prof. Porter whether he has calculated the  $I_3$  concentration he would expect under their experimental conditions, and therefore whether there is a real discrepancy here?

**Prof. G. Porter** (*Sheffield University*) said: The equilibrium constant of formation of  $I_3$  from I and  $I_2$  is estimated, from the recombination results, to be about  $4 \times 10^{-3} \exp(5000/RT)$  l. mole<sup>-1</sup>. Under the experimental conditions of Perlman and Rollefson (723-1274°K and 0.1-1 atm) this leads to a concentration of  $I_3$  somewhat less than the 0.3 mole % given by these authors as the lower limit of  $I_3$  which could have been detected.

**Dr. J. Keck** (*AVCO Res. Lab., Mass.*) said: I should like to point out that the variational theory<sup>2</sup> developed by the author also fits the observed recombination rates presented by Porter. In the temperature range from 300 to 500°K where the experiments were performed, the variational expression for the recombination rate constant given by eqn. (45) of ref. (1) is

$$k_r = k^B(0) = 2.0 \times 10^8 \sigma^2 (\exp(\varepsilon/RT) - 0.6) \text{ l.}^2 \text{ mole}^{-2} \text{ sec}^{-1}, \quad (1)$$

where  $\sigma$  is the range in Å and  $\varepsilon$  is the depth in kcal of the Lennard-Jones potential used to represent the interaction between an iodine atom and the chaperon. Note that the numerical factors in eqn. (1) are uniquely determined by the interaction potentials between the particles. The factor  $\exp(\varepsilon/RT)$  which gives the main temperature dependence of both the variational theory and the radical-molecule complex theory has its origin in the assumption common to both theories that IM is in equilibrium with I+M. A rough criterion for the validity of the assumption is that  $[R]/[M] \ll \exp(-\varepsilon/RT)$ .

The apparent negative activation energy implied by eqn. (1) is

$$\varepsilon_a = \varepsilon/[1 - 0.6 \exp(-\varepsilon/RT)]. \quad (2)$$

If we use the experimental values of  $\varepsilon_a$  to determine  $\varepsilon$  as Porter has done and choose a mean value of  $\sigma = 3.7$  Å determined from parameters given in Hirschfelder, Curtiss and Bird,<sup>3</sup> we obtain the results plotted in fig. 1.

It is clear that the variational theory fits the observations just as well as the radical-molecule complex theory. However, the former theory gives binding energies somewhat smaller than the latter. In the cases involving inert-gas chaperons, this leads to binding energies which are closer to those expected for the Van der Waals force and, therefore, seem more acceptable. In fact, considering the possibility<sup>4, 5</sup> of an additional small negative temperature coefficient in the pre-exponential factor of eqn. (1) due to lack of equilibrium in the vibrational degrees of freedom, it is possible that there is no additional force in these cases at all. In cases which do not involve inert-gas chaperons, there remains a clear indication of additional forces. This possibility was recognized by the author in his earlier work,<sup>2</sup> and it is for this reason that absolute calculations of rate constants were limited to inert-gas chaperons.

<sup>1</sup> *J. Chem. Physics*, 1941, **9**, 362.

<sup>2</sup> Keck, *J. Chem. Physics*, 1960, **32**, 1035.

<sup>3</sup> Hirschfelder, Curtiss and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954).

<sup>4</sup> Widom, *J. Chem. Physics*, 1960, **34**, 2050.

<sup>5</sup> Pritchard, *J. Physic. Chem.*, 1961, **65**, 504.

The reason for the difference in the binding energy predicted by the two theories is that the pre-exponential factor in the radical-molecule complex theory is proportional to the temperature, while that in the variational theory is nearly temperature independent. This in turn is associated partly with the fact that the variational theory leads to cross-sections which decrease with increasing temperature and partly with the fact that in the variational theory we have averaged over the *forces* which act on the particles, while in the radical-molecule complex theory, the average is over the relative *velocity* of approach of the particles.

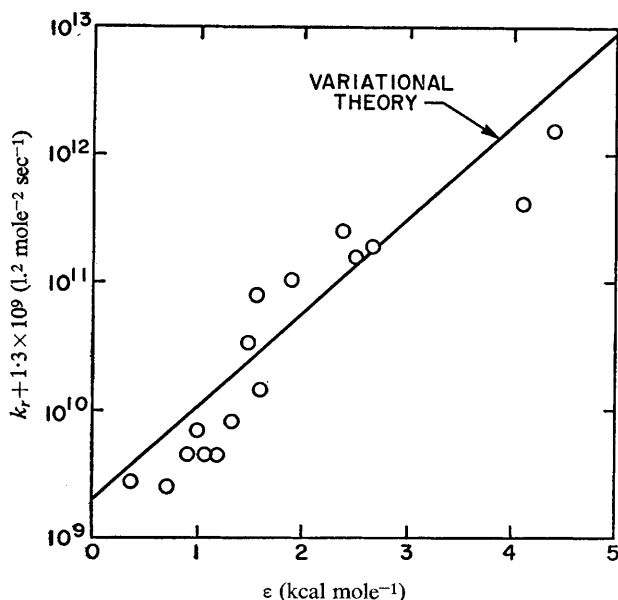


FIG. 1.—Comparison of experimentally observed recombination rate constants  $k_r$  for iodine in the presence of various chaperon molecules with curve predicted by the variational theory. The parameter  $\epsilon$  is the depth of the Lennard-Jones potential used to fit the observed temperature coefficient.

Although the agreement between theory and experiment exhibited in fig. 1 is very satisfactory in an overall sense, the assumption of a collision diameter independent of the chaperon molecule is certainly unrealistic. We have, therefore, analyzed the data to obtain the collision diameters as well as the binding energies with the objective of making more apparent possible correlations between these parameters and the character of the chaperon. The results are shown in fig. 2. The circles indicate the experimental values and the bars are theoretical values computed from data given in Hirschfelder, Curtiss and Bird on the assumption that iodine is equivalent to xenon. In obtaining the experimental values, we have multiplied eqn. (1) by a correction factor  $[\mu_{12}/(\mu_3 + \mu_{12})]^{0.9}$  suggested by the Monte Carlo trajectory calculations reported in the paper submitted to the Discussions by the author. While strictly speaking this correction was calculated only for the inert-gas chaperons, it probably has some validity even for complex chaperons and in any case it is not very large.

The most obvious trend in results is the tendency for simple molecules to have collision diameters somewhat smaller than the theoretical values. This does not seem unreasonable since the existence of an additional attraction between the iodine

and chaperon would certainly tend to move the minimum in the potential curve to smaller values of internuclear separation. For complex chaperons, the comparison can only be made for benzene in which case the experimental collision diameter is larger than the theoretical. Whether this is significant is not clear, but one possible explanation would be that the possibility of transferring energy to vibrational degrees of freedom in complex molecules makes them more efficient chaperons. This effect is not included in the present calculations.

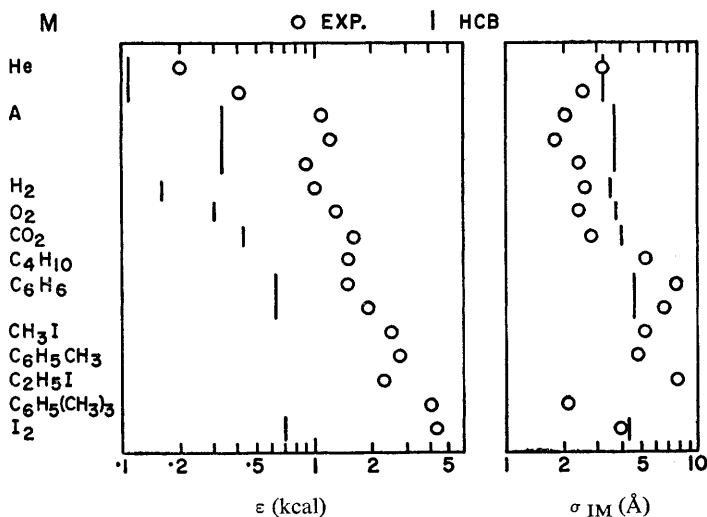


FIG. 2.—Lennard-Jones parameters for the interaction of iodine with various chaperon molecules *M*. The circles are the experimental values deduced from observations presented by Porter; the bars are the theoretical values obtained from data in Hirschfelder, Curtiss and Bird on the assumption that iodine is equivalent to xenon.

Although it is probably somewhat premature to take these observations too seriously, the author feels that use of refined theories in conjunction with reaction rate data is a potentially powerful method of obtaining information about the intermolecular forces which operate in chemical reactions. I am sure this feeling is shared by Prof. Porter and one purpose of these comments was to emphasize this point.

In concluding, I would like to point out some of the advantages of the variational theory over competing theories. First, it relates the reaction rate directly to the interaction potential without the usual uncertainty involving the choice of an effective cross-section which arises in most three-dimensional collision theories. Secondly, it includes all the classical reaction paths leading to recombination. Thirdly, it can be systematically improved using objective mathematical procedures. Finally, it can be applied in principle to any chemical reaction and is thus a promising basis for a unified theory of chemical reaction rates.

**Dr. F. T. Smith** (*Stanford Res. Inst., Calif.*) said: In using information on classical trajectories from large-scale computers, we must not forget that our problems are really quantal. The classical approximation is good for large quantum numbers (shall we say, for vibrations,  $n \geq 10$ ?), but this means large quantum numbers in *all* degrees of freedom. This condition is not often fulfilled.

As an example, take the exchange reaction  $A + BC \rightarrow AB + C$ , assuming an activation barrier. There are two restrictions to a classical treatment. First, the average